Defense Technical Information Center Compilation Part Notice

ADP011916

TITLE: The Influence of the Growth Conditions on the Elastic Properties of SrLaAlO4 and SrLaGaO4 Crystals Studied by Brillouin Light Scattering

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: International Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals Held in Zakopane, Poland on 9-12 October 2000

To order the complete compilation report, use: ADA399287

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP011865 thru ADP011937

The influence of the growth conditions on the elastic properties of $SrLaAlO_4$ and $SrLaGaO_4$ crystals studied by Brillouin light scattering

D. Kasprowicz[1], M. Drozdowski[1], A. Wronkowska[2], A. Pajączkowska[3]

[1]Faculty of Technical Physics, Poznań University of Technology, Poznań, Poland
[2]Institute of Mathematics and Physics, University of Technology and Agriculture, Bydgoszcz, Poland
[3]Institute of Electronic Materials Technology, Warszawa, Poland

ABSTRACT

Study of the optic and elastic properties of $SrLaAlO_4$ and $SrLaGaO_4$ crystals are presented. The investigated crystals were grown by Czochralski method. The elastic constants of $SrLaAlO_4$ and $SrLaGaO_4$ crystals at room temperature have been determined by Brillouin scattering method. Refractive indices have been measured independently by ellipsometry technique. The results are discussed in terms of the oxygen point defects, which can be created in the lattices of $SrLaAlO_4$ and $SrLaGaO_4$ crystals during the growth process.

Keywords: oxides, point defects, Brillouin scattering, ellipsometry

1. INTRODUCTION

$SrLaAlO_4$ (SLA) and $SrLaGaO_4$ (SLG) are applicated as substrates for high temperature superconducting thin films. SLA and SLG compounds crystallize in the perovskite – like, tetragonal $KNiF_4$ – type structure of I4/mmm space group. The structure of the crystal is built up of translationally equivalent layers formed by AlO_6 (GaO_6) octahedra and between the layers the Sr^{2+} and La^{3+} ions are randomly distributed in the sites of C_{4V} symmetry. There are two non-equivalent positions of oxygen atoms in the unit cell. The oxygen O2 is situated along the c-axis above Al^{3+}(Ga^{3+}) ion and the oxygen O1 situated in a-b plane.[1] The physical properties of SLA and SLG crystals have been studied intensively using different experimental method.[2-5] It was reported that the structure of SLG crystal is disturbed by the existence of the oxygen point defects which appear during the growth process. [6-10] In this paper we presents results concerning the influence of growing atmosphere on the optic and elastic properties of SLA and SLG crystals. The values of refractive indices n_o, n_e, elastic constants $C_{11} = C_{22}$, C_{33}, C_{44}, $C_{55} = C_{66}$, C_{12}, $C_{13} = C_{23}$ of SLA and SLG crystals, which were grown in different atmosphere, are compared. Cross sections of the phase velocities v for longitudinal (L) and transverse (T_1 and T_2) acoustic waves propagating in (001) plane of SLA and SLG crystals are presented. The results are discussed in terms of the oxygen point defects, which can be created in the lattices of SLA and SLG crystals during the growth process.

2. EXPERIMENT

SLA and SLG crystals used in our experiment were grown by Czochralski method at the nonstoichiometric proportion. The light yellow SLA and SLG crystals were grown in nitrogen atmosphere at the oxygen pressure of $4 \cdot 10^{-5}$ atm. The green color SLA and SLG crystals were obtained at the oxygen pressure higher than $5 \cdot 10^{-3}$ atm.[6] Samples of very good optical quality were cut in appropriate directions according to the imposed selection rules. For our measurements we used samples of sizes: 5mm x 4mm x 3mm, with faces perpendicular to the [100], [010], [001], [110], [101] directions. The Brillouin polarized spectra were taken in the standard 90^0 scattering geometry at room temperature. As a source of light we used λ = 488 nm line of an argon – ion laser operating on a single – mode. The scattered light was analyzed trough a piezoelectrically driven Fabry – Perot interferometer. The overall finesse (free spectral range divided by the instrumental full with at half maximum of the incident light) achieved was not less than 50.

Refractive indices of SLA and SLG crystals were obtained by applying variable angle ellipsometry. The ellipsometric azimuths ψ and Δ were determined at room temperature as a function of incidence angle φ for wavelength $\lambda = 488$ nm. The ellipsometer used was an automatic instrument of the rotating analyzer type from J. A. Woollam Company. The measurements were performed for φ ranging from 60° to 70° at an angular resolution of 0.1°. The accuracy of angle of incidence was ±0.005°.

3. RESULTS

The elastic stiffness tensor of SLA and SLG has six nonzero and non equal components: $C_{11} = C_{22}$, C_{33}, C_{44}, $C_{55} = C_{66}$, C_{12}, $C_{13} = C_{23}$.[11] In order to determine elastic constants from Brillouin scattering spectra suitable scattering geometry have to be chosen.[12] Using different scattering geometry we were able to study the propagation of the longitudinal (L) and transverse (T_1 and T_2) acoustic waves. The velocities v of a proper acoustic waves were calculated using Brillouin equation:

$$\Delta \nu_B = \frac{v}{\lambda}\sqrt{n_i^2 + n_s^2 - 2n_i n_s \cos\theta} \tag{1}$$

where: λ is the wavelength of the incident light, n_i, n_s are refractive indices for the incident and scattered light, respectively and θ is the scattering angle, $\Delta \nu_B$ is the Brillouin shift. The elastic constants are calculated from the solution the equation of the motion which is given by:

$$\left| C_{ijkl} q_j q_k - \rho v^2 \delta_{ij} \right| = 0 \tag{2}$$

where: q_j, q_k are the direction cosines of the acoustic wave propagation , C_{ijkl} are the elastic constants and ρ is the density of crystal. The direction of phonons q and corresponding ρv^2 as a function of the elastic constants for longitudinal (L) and transverse (T_1 and T_2) acoustic waves are summarized in the Table 1.

Table 1. The direction q, expression for ρv^2 as a function of the elastic constants C_{ij} and values of velocities v for longitudinal (L) and transverse (T_1 and T_2) acoustic waves propagating in yellow and green SLA and SLG crystals. The density $\rho = 5.924$ g/cm^3 for SLA and $\rho = 6.389$ g/cm^3 for SLG.

q	mod	ρv^2	SLA yellow v [m/s]	SLA green v [m/s]	SLG yellow v [m/s]	SLG green v [m/s]
[110]	**T_2**	C_{44}	4000	4010	3670	3770
$[\bar{1}10]$	**T_2**	C_{44}	4000	4010	3650	3780
[110]	**L**	$\frac{C_{11}+C_{12}+2C_{66}}{2}$	7120	7130	6340	6420
[101]	**T_2**	$\frac{C_{44}+C_{66}}{2}$	4260	4300	3790	3820
$[\bar{1}01]$	**T_2**	$\frac{C_{44}+C_{66}}{2}$	4260	4280	3780	3810
[011]	**T_2**	$\frac{C_{44}+C_{66}}{2}$	4330	4270	3790	3810
$[0\bar{1}1]$	**T_2**	$\frac{C_{44}+C_{66}}{2}$	4240	4260	3790	3870
[101]	**L**	$\frac{(C_{11}+C_{33}+2C_{44})+\sqrt{(C_{11}-C_{33})^2+4(C_{13}+C_{44})}}{4}$	6750	6800	6460	6540
[011]	**L**	$\frac{(C_{11}+C_{33}+2C_{44})+\sqrt{(C_{11}-C_{33})^2+4(C_{13}+C_{44})}}{4}$	6770	6820	6570	6460
[100]	**L**	C_{11}	6630	6540	6130	6350
[001]	**L**	C_{33}	6620	6660	6300	6320

The refractive indices of yellow and green SLA and SLG which are needed for the calculation of the elastic constants using Brillouin scattering have been determined by applying variable angle ellipsometry. It is an optical technique based on analyzing the polarization changes caused by reflection of light at the interface between two dielectric media. The components of the electric field **E** parallel (E^p) and perpendicular (E^s) to the plane of incidence are reflected and transmitted to a different degree resulting in polarization dependent reflection and transmission coefficients $r^{p,s}$ and $t^{p,s}$, respectively, which are described by Fresnel's equations.[13] The basic quantity measured is the complex reflection ratio defined as:

$$\mu = \frac{r^p}{r^s} \tag{3}$$

that can be expressed through the ellipsometric azimuths ψ and Δ in the following form:

$$\mu = tan\psi \exp(i\Delta) \tag{4}$$

where $i = \sqrt{-1}$. In the last equation $tan\psi$ contains ratio of the electric field amplitudes of the incident and reflected light beams, and Δ is the reflection induced difference in phase change between the two field components. Since ellipsometric azimuths are dependent on a wavelength λ, and angle of incidence of light, φ, such a measurement can be used for characterization of the optical properties of the entire system. By ellipsometry it is possible to directly determine, for a given photon energy, the complex refractive index N = n - ik of an isotropic material with a perfectly smooth surface. In the case of an anisotropic sample, for uniaxial crystal, two measurements of ellipsometric parameters for the high symmetry orientations of the optic axis with respect to the plane of incidence are necessary to calculate the principal components of the dielectric tensor.[13-14] In general, reflection of light from anisotropic or chiral media is determined by the four reflection amplitude coefficients (r^{pp}, r^{ss}, r^{ps}, and r^{sp}).

An alternative method of finding the ordinary n_o and extraordinary n_e indices of refraction of uniaxial crystal is based on the identification of an analogous the Brewster angle or pseudo-Brewster angle when the sample is absorbing the applied radiation. It means that p-polarized light is not reflected at the Brewster angle of incidence φ_B, thus giving $\psi = 0$ ($r^{pp} = 0$). Only special orientations of uniaxial crystals are known for which an explicit formula exists for the angle φ_p, at which no p-polarized light is reflected when the incident light has the p-polarization.[15] When the optic axis (c-axis) is normal to the plane of incidence the polarizing angle φ_p is equal to the Brewster angle for an isotropic medium of refractive index n_o by

$$tan\,\varphi_p = \frac{n_o}{n} \tag{5}$$

where n is the refractive index of ambient. The extraordinary index of refraction can be found using the following formula:

$$n_e = \sqrt{\frac{\left(n_0^2 - 1\right) tan^2\varphi_p^{'}}{n_0^2} + 1} \tag{6}$$

which applies for the case when the optic axis lies in the plane of incidence parallel to the interface and the measurements are made in air.

In this experiment the polarizing angles φ_p and φ'_p were derived from $\psi(\varphi)$ $\Delta(\varphi)$ curves for high-symmetry orientation of the crystal samples with c-axis perpendicular and parallel to the plane of incidence, respectively. They were determined as the angles of incidence for which $\psi = 0$ (or it has minimum) whereas $\Delta = \pi/2$. In this way, it is possible to find the Brewster angles with accuracy limits not exceeding ±0.05°. The extinction coefficients k_o and k_e were determined using the ellipsometric azimuths measured for the high-symmetry orientations of c-axis with respect to the plane of incidence.

In Table 2 we present values of refractive indices n_o and n_e together with extinction coefficients k_o and k_e of yellow and green SLA and SLG crystals. The accuracy of refractive indices estimated is ±0.0025.

The values of elastic constants C_{ij} of yellow and green SLA and SLG crystals determined at RT by Brillouin scattering are listed in the Table 3. The accuracy in the estimation of elastic constants is no more than 2%.

The phase velocities of longitudinal (L) and transverse (T_1 and T_2) elastic waves propagating in (001) plane for SLA and SLG crystals have been calculated using C_{ij} constants. Cross sections of the phase velocities of the elastic waves propagating in (001) plane for yellow and green SLA and SLG crystals are shown in Fig.1 and Fig.2.

Table 2. The values of refractive indices n_o and n_e, extinction coefficients k_o and k_e of yellow and green SLA and SLG crystals.

crystal	n_o	n_e	k_o	k_e
SLA – yellow	1.9754	1.9960	0.093	0.102
SLA – green	1.9685	1.9912	0.121	0.153
SLG – yellow	2.0189	2.0530	0.118	0.130
SLG – green	2.0010	2.0416	0.144	0.172

Table 3. Elastic constants C_{ij} of yellow and green SLA and SLG crystals at RT (in 10^{10} N/m^2)

crystal	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
SLA – yellow	25.73	10.25	9.18	25.93	9.45	12.06
SLA – green	25.31	10.55	9.96	26.30	9.51	12.20
SLG – yellow	24.04	8.61	11.67	25.32	8.94	9.37
SLG - green	25.73	7.97	10.80	25.49	9.09	9.51

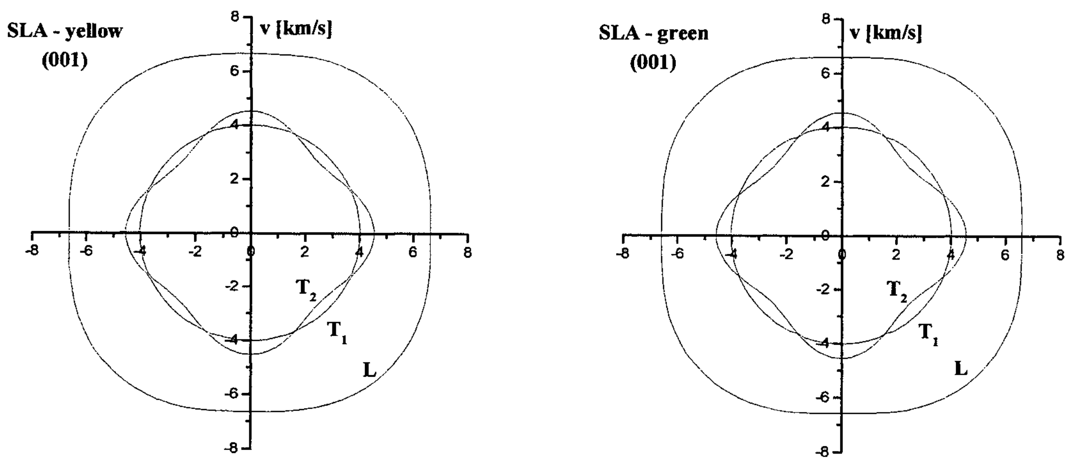

Fig.1. Cross sections of the phase velocities v (km/s) for longitudinal (L) and transverse (T_1 and T_2) acoustic waves propagating in (001) plane for yellow and green SLA crystals.

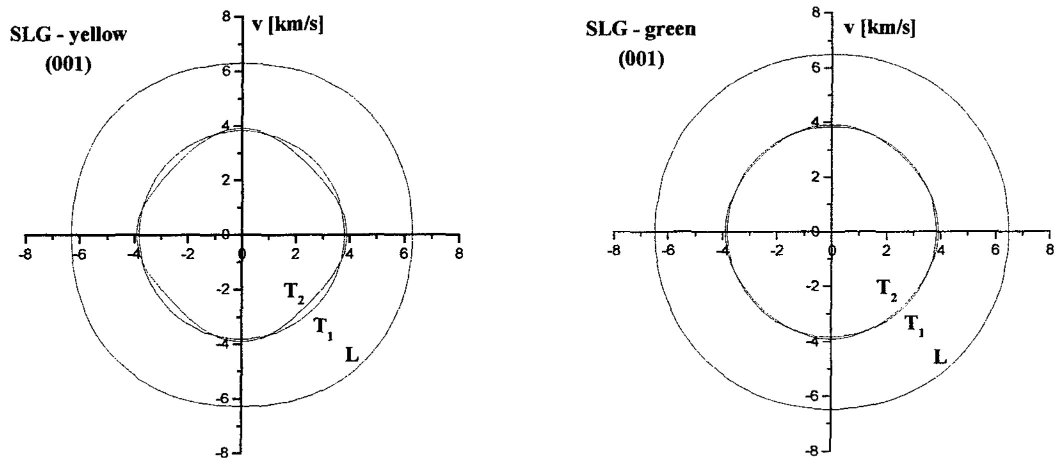

Fig.2. Cross sections of the phase velocities v (km/s) for longitudinal (L) and transverse (T_1 and T_2) acoustic waves propagating in (001) plane for yellow and green SLG crystals.

4. CONCLUSIONS

Both, SLA and SLG single crystals are characterized by larger the n_e than n_o values for wavelength $\lambda = 488$ nm. The refractive indices of green colored samples are lower than those determined for yellow colored ones. As it can be seen from Fig.1. the propagation of the longitudinal (L) and transverse (T_1 and T_2) acoustic waves in (001) plane is typical for tetragonal symmetry both, for yellow and green SLA crystals. However, we observe the disturbed propagation of the longitudinal (L) and transverse (T_1 and T_2) acoustic waves propagating in (001) plane for yellow and green SLG crystals Fig.2. Moreover, for green SLG crystal the degeneracy of the transverse (T_1 and T_2) modes along the [100] and [010] directions occurs. The observed anomaly in the acoustic waves propagation for yellow and green SLA and SLG crystals is probably associated with the displacement of the oxygen ions from their original positions in the crystal lattice. This phenomena can lead to the distortion of the oxygen octahedral, which finally leads to a lower symmetry of the crystal structure from the tetragonal I4/mmm. Moreover, the concentration of oxygen defects depends on the oxygen pressure during the growth process which is visible as the increase some of the elastic constants (Table 3) for green SLG crystals
The results obtained are consistent with our previous study of the elastic and elastooptic properties.

ACKNOWLEDGEMENTS

Authors wish to thank Department of Physics and Measurement Technology Linköping University and individually Prof. Hans Arwin for permission of use their automatic ellipsometer and measurement assistance.
This work has been sponsored by the Research Program PB-64-003/2000/BW

REFERENCES

1. J. F. Britten, H. A. Dabkowska, A. D. Dabkowski, J. E. Greedan, J. L. Campbell, W. J. Teesdale, *Acta Cryst.* **C51**, pp.1975, 1995.
2. A. Pajączkowska, A. Glubokov, „Synthesis, growth and characterization of tetragonal $ABCO_4$ crystals.", *Prog. Cryst. Growth and Charact.*, **36**, pp. 123-162, 1998.
3. A. Gloubokov, R. Jabłoński, W. Ryba-Romanowski, J. Sass, A. Pajączkowska, R. Uecker, P. Reiche, „On the preparation and crystal growth of $SrLaAlO_4$", *J. Cryst. Growth.*, **147**, pp. 123-129, 1995.
4. S. Kamba, E. Buixaderas, A. Pajączkowska, "Polarized Infrared Reflectivity Spectra of $SrLaAlO_4$ and $SrGaAlO_4$ single crystals." *Phys.Stat. Sol. (a),* **168**, pp. 317-324, 1998.
5. M. Drozdowski, A. Pajączkowska, D. Kasprowicz, P. Ziobrowski, A. Kłos, „Study of the elastic properties of $SrLaAlO_4$ and $SrGaAlO_4$ single crystals by Brillouin light scattering.", *Cryst. Res. Technol.*, **31**, pp. 361-364, 1996.

6. A. Pajączkowska, A. Kłos, D. Kasprowicz, M. Drozdowski, „Influence of oxygen on the growth of some oxide crystals.", *J. Cryst. Growth.*, **198/199**, pp. 440-443, 1999.
7. W. Ryba-Romanowski, S. Gołąb, I. Sokólska, W. A. Pisarski, G.Dominiak-Dzik, A. Pajączkowska, M. Berkowski, „Anisotropy of optical properties of $SrLaAlO_4$ and $SrLaAlO_4$:Nd", *J. Alloys. Comp.*, **217**, pp. 263-267, 1995.
8. M. Drozdowski, J. Domagała, M. Kozielski, M. Szybowicz, A. Pajączkowska, „ Temperature study of lattice constants and Raman scattering of $SrGaAlO_4$ single crystal.", *Sol. St. Commun.,* **96**, pp. 785-788, 1995.
9. M. Kozielski, A. Jezierski, D. Kasprowicz, M. Szybowicz, "Band structure of $SrLaAlO_{3+\delta}$ and $SrLaAlO_{3+\delta}$.", *Cryst. Res. Technol.*, **34**, pp. 715-718, 1999.
10. D. Kasprowicz, M. Drozdowski, A. Pajączkowska, P. Ziobrowski, A. Kłos, „Anisotropy of the elastooptic properties of SLA and SLG crystals studied by Brillouin scattering.", *Cryst. Res. Technol.*, **34**, pp. 703-707, 1999.
11. J. F. Nye, *Physical Properties of Crystals*, Oxford, Clarendon Press, 1957.
12. R. Vacher and L. Boyer, „„Brillouin scattering: A tool for the measurement of elastic and photoelastic constants.", *Phys. Rev.*, **B6**, pp. 639-673, 1972.
13. R. M. A. Azzam, N. M. Bashara, *Ellipsometry and polarized light*, North-Holland, Amsterdam-New York-Oxford, 1977.
14. A. G. Pahomov, B. J. Posylnyi, A. F. Konstantinova, *Ellipsomietria – mietod issledovania povierchnostii,* Nauka, Novosibirsk, 1983.
15. J. Lekner, "Reflection by uniaxial crystals: polaryzing angle and Brewster angle.", *J. Opt. Soc. Am.*, **A 16** , pp. 2763, 1999.